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# Parameters to take into account when developing a new thermochemical energy storage system

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**Abstract**

Thermal energy storage by chemical reactions is one of the most suitable energy storage systems for buildings and industrial applications due to the wide range of working temperatures as well as the high energy storage density provided. Developing and characterizing chemical reactions is now one of the most promising areas of research. Chemical heat pumps are one of the systems used when chemical reactions are utilized as thermochemical energy storage technology. Nevertheless, the main problem to implement this technology is found in the material behaviour within the reactors used. Therefore, material and reaction characterization have been identified as key issues to design a proper system. The main goal of this paper is to highlight the parameters to take into account previous to the design.



*Keywords*: Thermal energy storage (TES); thermochemical materials (TCM); gas-solid kinetics.

## 1. Introduction

Thermal energy storage (TES) is an interesting technology in terms of efficient energy use. There are three main types of TES systems known as sensible, latent and chemical. Chemical TES involves storing heat within thermochemical material (TCM) molecular bonds. This is becoming popular due to the wide range of working temperatures and the high energy storage density provided when comparing to sensible

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and latent heat. Furthermore, there are almost no energy losses when storing heat chemically [1]. Thus, it has potential to be used for buildings and industrial applications, mainly as a technology for long-term thermal storage applications [2-4].

The systems implementing TCM allow absorbing solar heat during summer months, to store it seasonally, and to release it during winter. One of these systems is a chemical heat pump (CHP) and it is shown as an efficient energy utilization technology [2]. The operation of a CHP involves a TCM working in a cycle. This is a key issue that should be taken into account as materials should be kept in properties if the expected storage capacity is wanted to be achieved [5]. Also, intermediaries and phase change can take place when working with TCM.

The main problem to implement this technology is found in the material behavior within the reactors used. As pointed out [4], there are some published results that are inconclusive. This ambiguity may be due to improper or insufficient chemical reaction and reactant/product characterization. Developing and characterizing proper chemical reactions for thermochemical systems is now one of the most promising areas of research.

Different systems have been studied so far, with applications in different climates [2]. Most studied specific systems are considered in this paper in order to evaluate from bibliographic data: first the crystallographic change, second the solubility of the materials involved (reactant and product), and third, guidance for kinetic data acquisition and evaluation of the reactions presented.

## 2. Materials

Systems considered in this paper are reversible gas-solid reactions. Alkaline inorganic solid compounds which react with water, in gas state, have been chosen. Reaction systems can be distinguished in two groups (1) the ones that change from oxide to hydroxide: CaO-$Ca(OH)_2$ and MgO-$Mg(OH)_2$, and (2) those that change from a hydrated form to another, like $CaSO_4 \cdot xH_2O$, $MgSO_4 \cdot xH_2O$, $CaCl_2 \cdot xH_2O$, and $MgCl_2 \cdot xH_2O$ (x=0,1/2,1,..n).

## 3. Results and discussion

### *3.1 Crystallographic structural change*

In solid state reactions, some parameters should be taken into account when characterizing the reaction, such as the crystal structure change [6]. When the oxides considered here react with water vapor, crystalline structure change from cubic to hexagonal. While the change from anhydride calcium sulfate to the dihydrated form means a change from orthorhombic to monoclinic structure. The reaction enthalpy of the first structure change is one tenth of the second. Other reactions have other crystallographic changes (Table 1).

On the other hand, a key factor that may influence energetic values is the water molecule stability within the crystalline solid structure [20]. If the anion involved has high electron density and its crystalline structure is stable due to hydrogen bonds formation, the hydration enthalpy value is higher, as may be seen in Table 1 (hydration of $MgSO_4$ vs. $MgCl_2$). Nevertheless, there is not a common pattern hence each reaction should be considered by itself.

Table 1. Reaction Enthalpy and crystallographic change of materials studied here

| Reactant / Product | | Enthalpy ($T^a$) (kJ/g)* | Crystallographic change |
|---|---|---|---|
| CaO | $Ca(OH)_2$ | 2.00 (505 ºC) [7] | Cubic to Hexagonal |
| MgO | $Mg(OH)_2$ | 2.01 (350 ºC) [8] | [11-14] |
| $CaSO_4$ | $CaSO_4 \cdot 2H_2O$ | 14.86 (0ºC) [9] | Orthorhombic to Monoclinic [15,16] |
| $MgSO_4$ | $MgSO_4 \cdot 7H_2O$ | 28.17 (0ºC) [10] | Orthorhombic to Orthorhombic [9,17] |
| $MgCl_2$ | $MgCl_2 \cdot 6H_2O$ | 1.98 (0ºC) [9] | Hexagonal to Monoclinic [18,19] |

### *3.2 Solubility*

When solid inorganic salt hydrates and oxides/hydroxides are used as TES materials, they are not supposed to dissolve in liquid water; hence they should be available in solid state. As mentioned above, water is considered in gas state when reacting but after cycling it several times dissolution, which entails liquid water, can take place. Actually, durability of those systems has been widely studied although never related to solubility [21,22]. Kato et al. [21] state that durability of $MgO/H_2O$ is related to the material appearance (pellets, powder, etc.) and also to the impurities found in the material. Lin et al. [22] show that CaO hydration rate decreases with increasing number of hydration cycles, since crystal growth and specific surface area reduces by the progression of cycles. Only Hui et al. [23], mention solubility in their calculations for a TES system. Khawam and Flanagan [24] recommend studying the solubility of each chemical involved in a CHP, as hydrates may change their state of hydration producing forms with different solubility characteristics.

Figure 1 presents solubility vs. temperature of some of the different compounds considered in this paper [25]. Figure 1 shows that $CaCl_2 \cdot xH_2O$ are highly soluble. While, $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ are not soluble in water. Magnesium hydrated compounds have similar solubility, being comparable to that of $CaCl_2 \cdot 6H_2O$. This information corroborates the hypothesis that solubility in water of materials is an important property to consider.

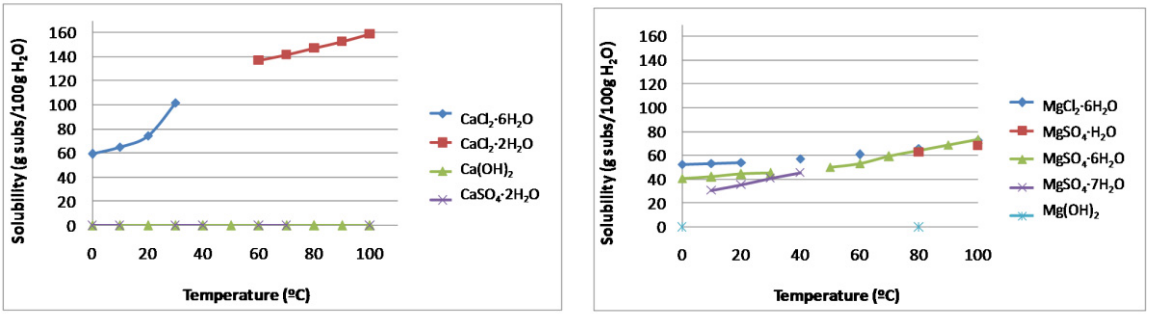


Fig. 1. (a) Calcium compounds solubility; (b) Magnesium compounds solubility

### *3.3 Kinetic study*

When working with reversible solid-state reactions, the kinetic study should not be avoided even if experimental data from other studies is available. Kinetic steps may change depending on solid state features (crystal structure, particle morphology, etc.), as has been discussed above, and also on the reaction conditions (pH, rate of mixing, temperature, pressure, etc.) [26,27].

However, several published papers related to thermochemical energy storage take data from other studies which may not be in the same experimental conditions and/or reactant morphology [4,23,28,29].

According to [27], several researchers obtain kinetic data from thermal analysis methods such as thermogravimetry (TGA), differential scanning calorimetry (DSC), and differential thermal analysis (DTA).

Some models, such as the shrinking core model, the highly porous model, and the porous reactant model, have been proposed and commonly used for gas-solid reaction systems. However, no simple explanation based on one of these models alone could predict the whole process of the hydration, which suggests that the hydration occurs via several processes [30]. In Table 2, several models and systems suggested by different authors are presented.

Table 2. Kinetic models suggested by different authors

| Authors, year | System | Model | Rate equation |
|---|---|---|---|
| Kato et al. 1996 [30] | $MgO/Mg(OH)_2$ | Empirical model based on four steps mechanism. | $F_h = - \ln (X_e-X)$ |
| Lin et al. 2006 [22] | $CaO/Ca(OH)_2$ | Shrinking core model with constant size particles | $F_h = -\ln (1-X)$ |
| Lee et al. 1986 [31] | $CaSO_4/CaSO_4 \cdot 1/2H_2O$ | Grain model | $F_h = 1-(1-X_n)^{1/3}$ |

In order to design the reactor in which the solid-state reaction will take place, a reliable kinetic model should be obtained. Kinetic experts alert researchers of the complexity of the reactions when obtaining kinetic data from thermal analysis of solid-gas reactions [26,27]. They also offer recommendations for performing analysis and interpreting their results. Briefly, the most important steps to characterize the reaction properly are [26,27]:

a) Solid characterization

Solid-state kinetics evolved from homogenous kinetic principles. However, applications of these kinetic principles are different because of the differences between solids, solutions, and gases. For example, particle size, interface advance, and geometric shape are variables unique to heterogeneous reactions and have no equivalent in homogenous reactions [26]. When identifying a kinetic model it is essential to include information about solid changes in textures, structures and bonding, this could be assessed by microscopy, crystallography and spectra, respectively. If nucleation, growth, or gas diffusion is visually observed microscopically, such an observation can support a nucleation or diffusion model obtained from statistical fitting. The conclusions drawn from statistical fitting can be further substantiated by these complementary methods, especially X-ray diffraction.

b) Experimental set-up

The rate of reaction is found by measuring some properties of a reactant or a product at different times after the start of the reaction; following the change in amount of reactant and/or product by titration, determining the volume of gas formed, following the change in mass, etc.

The decision of accepting the direct relation between physical parameter (mass, heat flow, etc.) and product formation or reactant disappearance should be thought carefully as intermediates may be appearing or phase change could take place.

To obtain meaningful kinetic conclusions, data must be based on several heating rates [26,27] and different reaction conditions. Figure 2 shows that data may be obtained by performing isothermal or non-isothermal experiments.

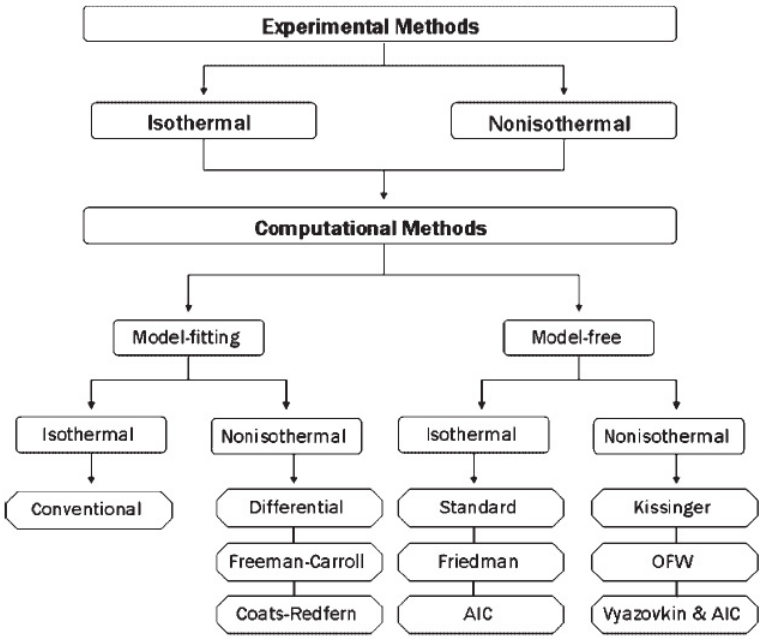


Fig. 2. Methods for studying solid-state kinetics [24]

c) Data evaluation

The choice of a model is generally based on statistical fits of mathematical models to data. However, model selection should also be supported, when possible, by complementary procedures such as microscopy, spectroscopy, X-ray diffraction, product analysis, evolved gas analysis, etc.

Also, sufficient accurate data must be obtained across the complete reaction. Plus, reproducibility of data obtained is important to enable the accuracy of kinetic parameters.

Once data are accurately obtained, in order to evaluate kinetic parameters, such as activation energy, different methods are available (Figure 2). Model-free methods allow the evaluation of the activation energy without determining the reaction model whenever the process can be approximated as single-step kinetics. If this condition cannot be satisfied, model-fitting methods should be used [27]. Unlike

isoconversional methods (model-free), the model-fitting methods are capable of identifying multi-step reaction models suitable for the description of complex kinetics.

To substantiate all above mentioned, an example of one specific system, CaSO4·2H2O/CaSO4, is shown [6] (Figure 3).

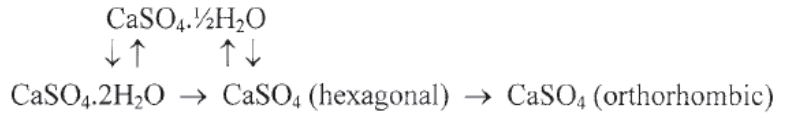


Fig. 3. Calcium sulphate dehydration

The kinetics and mechanisms of this system are complicated and depend on reaction conditions. For example, below 383 K, $CaSO_4 \cdot 2H_2O$ dehydration proceeds by nucleation and boundary control reaction, whereas above this temperature the rate is determined by diffusion.

Taking into consideration that the hemihydrate ($Ca_2SO_4 \cdot 1/2H_2O$) has α and β forms that are distinguished as different hydrates with α-$0.67H_2O$ and β-$0.5H_2O$, dehydration of the α-hemihydrate depends on reaction conditions below 383 K. Above 388 K, water losses from both α and β hemihydrates are diffusion controlled. The calculated magnitudes of activation energy ($E_a$) extended from about 40 to 120 kJ/mol so that the behavior pattern is not concisely summarized and includes an influence from water pressure.

$CaSO_4 \cdot 2H_2O$ dehydration below 425 K and at low pressure yields γ-$CaSO_4$. This deceleratory reaction was studied between 324 and 371 K, using single crystals that have a layered structure. The rate of interface advance in the (010) crystallographic direction is controlled by the diffusive migration of $H_2O$ across the solid product layer. In contrast, advance in the (001) direction is determined by the chemical step ($E_a$= 82 kJ/mol).

Paulik et al. [32] draw attention to the variations in rate evolution that result from changes in reaction conditions. According to [6], $CaSO_4 \cdot 2H_2O$ dehydrations literature is reviewed and it was concluded that not all inconsistencies had yet been resolved. There is no evidence for the occurrence of possible melting at 311 or at 366 K, predicted thermodynamically, but water loss yields the hemihydrate at about 400 K and anhydrous $CaSO_4$ above 440 K.

## 4. Conclusions

Three important factors were considered in this paper in order to achieve the expected design of the technology implementing TCM.

Solid characterization of the solids involved in the reaction under study should be done, before and after reacting. For instance, crystallographic structure change, water stability within crystal structure, particle size, impurities, etc. This could be assessed by microscopy, crystallography, spectra, etc. When characterizing the solid in depth, the observations highlight the processes that have occurred. The more reliable is the obtained kinetic model if the processes that rule the reaction (nucleation, diffusion, etc.) are known.

Another property considered is solubility of chosen systems in water. It can be concluded that solubility of each solid implicated is an important parameter and should be evaluated within temperature work range. As TCM usually work in a cycling technology, this could culminate in dissolution thus reaction rate will decrease.

Finally, the proper pathway to obtain a kinetic model for a reaction in specific working conditions, as temperature and pressure is shown. Solid characterization, suitable data acquisition and proper data evaluation are the main steps to be considered. Each reversible reaction which is wanted to perform in a reactor must be first properly characterized in the specific operation conditions.

Technology status of chemical energy storage is generally not available but undergoing research and pilot project test [1] therefore preliminary steps as parameters presented in this paper should be taken into account to reach the theoretical yield of the developed technology.

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